

**INTERACTION OF PLASMA-SPRAYED $\text{YBa}_2\text{Cu}_3\text{O}_x$ COATINGS
WITH ALUMINA SUBSTRATES**

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ABSTRACT

Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_x$ coatings can be obtained by plasma spraying. Since the as-sprayed coatings do not have an appropriate crystalline structure and are not superconducting, a thermal treatment must be done for crystallizing them in the appropriate $\text{YBa}_2\text{Cu}_3\text{O}_x$ phase. During heat treatment, reactions between the substrate and coating occur and in some cases, may prevent superconducting properties to be obtained. In the present study, $\text{YBa}_2\text{Cu}_3\text{O}_x$ coatings have been deposited on alumina substrates by plasma spraying and heat treated under flowing oxygen at 950°C for different periods of time. The modification in coating microstructure has been investigated after different heat treatments. A degradation mechanism of superconducting coatings is proposed.

INTRODUCTION

Since the discovery of the new high T_c ceramic superconductors, a lot of work has been done on the processing of those new oxides in order to develop large scale industrial applications. The processing of the ceramic is intricate due to the brittleness of the oxide and the necessity to adjust its oxygen content by heat treatment.

The plasma spraying technique is an industrially viable coating technique which can be used for the deposition of superconducting $YBa_2Cu_3O_x$ coatings on various substrates (1-4). The technique permits to rapidly deposit coatings with thicknesses ranging from 10 μm to few millimeters on large surfaces.

As-sprayed $YBa_2Cu_3O_x$ coatings do not exhibit superconducting properties at liquid nitrogen temperature. The inadequate crystalline state and/or the low oxygen content of the as-sprayed material are responsible for that loss of superconductivity. A thermal treatment is thus required to restore the superconducting $YBa_2Cu_3O_x$ phase. During this heat treatment period, interaction between the substrate and coating may occur and degrade the superconducting properties. This could be particularly important for very thin coatings. Coatings applied by other techniques (e.g. thermal evaporation, sputtering, etc.) must also be heat treated after deposition and a similar degradation has been noted (5-9).

In this paper, the interaction of plasma-sprayed $\text{YBa}_2\text{Cu}_3\text{O}_x$ coatings with polycrystalline alumina substrates is discussed. This substrate has already been reported to react with $\text{YBa}_2\text{Cu}_3\text{O}_x$ coatings (5-7). The present study was aimed at studying modifications in coating microstructure that occur upon heat treatment in order to select optimum spraying parameters and heat treatment conditions.

EXPERIMENTAL PROCEDURE

The spraying powder has been prepared by mixing 99.999% purity powders of BaCO_3 , Y_2O_3 and CuO and reacting them at 950°C for 12 hours in flowing oxygen. The reacted product was grounded, sieved to $-38\text{ }\mu\text{m}$ and then heat treated again at 950°C for 12 hours in flowing oxygen. Thereafter, the reacted material was grounded again and the $-63\text{ }\mu\text{m}$ $+38\text{ }\mu\text{m}$ size fraction was sorted for spraying. Plasma spraying was carried out with a commercial equipment at a power of 22 kW using argon as arc and powder feeding gases. The stand-off distance was 7.6 cm.

Thermal treatments consisted in heating sprayed coatings from room temperature to 950°C in about 100 minutes in flowing oxygen, holding them at this temperature for various periods of time and cooling them in the furnace.

Superconducting properties of the heat treated coatings were examined by resistivity measurements carried out by a four-probe method. Quantitative energy dispersive X-ray (EDX) analyses were performed with a

Tracor instrument. X-ray patterns have been obtained with $\text{Cu K}\alpha$ radiation.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of coating surfaces heat treated for different periods. The as-sprayed coating pattern (Figure 1-a) has a broad peak around 30 degrees and only few unidentified sharp peaks. The as-sprayed coating is not superconducting above liquid nitrogen temperature.

Figures 1-b, 1-c and 1-d show the X-ray diffraction patterns of coatings heat treated for 15 minutes, 30 minutes and 6 hours, respectively. These patterns indicate that coatings crystallize to mainly form the $\text{YBa}_2\text{Cu}_3\text{O}_x$ phase. Secondary phases become important after 6 hours as indicated by the extra peaks between 29 and 32 degrees and between 34 and 38 degrees in Figure 1-d. These peaks correspond to the non-superconducting green phase Y_2BaCuO_5 . The patterns of samples heat treated for 15 and 30 minutes (Figures 1-b and 1-c) are not significantly different indicating that their compositions are very similar.

Figure 2 shows the normalized resistivity (ρ/ρ_0) versus temperature curves for the three heat treated samples. It must be noted that the critical temperature of samples decreases as the heat treatment period increases. The zero resistance temperatures are found at about 87K and 80K for samples heat treated for 15 and 30 minutes, respectively. The 6

hour heat treated sample does not show a complete superconducting transition above liquid nitrogen temperature. At 77 K, its resistivity is about one third of its resistivity at the transition onset. The sample resistivities at 273 K are about 15 mohm-cm after the 15 and 30 minute heat treatments and about 65 mohm-cm after the 6 hour heat treatment. It is worth mentioning that the resistivity decrease from room temperature to 100 K is less pronounced for longer heat treatments. Moreover, this decrease is not linear with temperature as normally observed for a pure $\text{YBa}_2\text{Cu}_3\text{O}_7$ material.

Figure 3 shows a micrograph of an as-sprayed $\text{YBa}_2\text{Cu}_3\text{O}_x$ coating on an alumina substrate. The coating porosity is low indicating that most of the particles were melted during their passage into the plasma. Quantitative EDX analyses have been performed on an as-sprayed coating and on a pure $\text{YBa}_2\text{Cu}_3\text{O}_x$ compact of superconducting powders sintered in pure oxygen. Local analyses have been performed on each sprayed sample to determine a possible change in stoichiometry of the metallic elements. No significant change has been noted.

Low aluminium concentrations are difficult to quantify when a high quantity of yttrium is present due to the proximity of the Al K_α and Y L_α peaks in the EDX spectrum. Therefore, low aluminium concentrations determined by EDX analysis in yttrium rich phases must be considered as approximate.

Figure 4-a shows the micrograph of a superconducting coating heat

treated for 15 minutes. Some cracks and porosities are generated within the coating during heat treatment. EDX mappings of yttrium, barium and copper for the coating illustrated in Figure 4-a are shown in Figures 4-b, 4-c and 4-d, respectively. According to these figures, five distinct phases, denoted in Figure 4-a, are distributed within the coating. The elemental composition of the most important phases are given in Table 1. The principal phase (phase 1) contains Y, Ba and Cu and corresponds to the superconducting $\text{YBa}_2\text{Cu}_3\text{O}_x$ phase. In that principal phase, quantitative EDX analyses have been performed in regions near the coating-substrate interface and near the coating surface. The results of these analyses, also given in Table 1, indicate that the aluminium concentration is more important near the interface. The second phase (phase 2) is richer in yttrium and its composition corresponds to Y_2BaCuO_5 (Table 1). Since large zones of Y_2BaCuO_5 were not detected in the as-sprayed coatings, they have grown during the 15 minute thermal treatment. The phase 3 is only found at the coating-substrate interface and is mainly composed of aluminium and barium (Table 1). Its copper content is very low and decreases near the alumina surface. The copper rich phase (phase 4) is mainly distributed in the vicinity of the interface between the $\text{YBa}_2\text{Cu}_3\text{O}_x$ and Al-Ba oxide phases and also in small areas within the coating. Finally, phase 5 is composed of barium and copper and is apparent only in few small spots on the micrograph of Figure 4-a.

Figures 5-a to 5-d show a micrograph and the corresponding metallic element mappings for a 6 hour heat treated coating. The compositions of the phases denoted in Figures 5-a are given in Table 2. The phases

observed in the coating heat treated for 15 minutes are also present in the coating heat treated for 6 hours with the exception of Ba-Cu oxide phase (phase 5) that is not observed in the latter coating. As noted above, the aluminum content of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ phase is higher near the alumina interface than near the surface of the coating. An important difference between a coating heat treated for 15 minutes and a coating heat treated for 6 hours is the relative proportion of each phase. In particular, the amount of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ phase decreases with longer heat treatment.

It has been shown that the aluminium incorporation in $\text{YBa}_2\text{Cu}_3\text{O}_7$ compound decreases its superconducting transition temperature T_c and increases its room temperature resistivity (10,11). EDX analyses performed on coatings heat treated for 15 minutes and 6 hours reveal the presence of an important aluminium concentration level in the $\text{YBa}_2\text{Cu}_3\text{O}_x$ phase, particularly near the alumina interface. For sprayed coatings, the T_c decrease and the room temperature resistivity increase with the duration of heat treatments are related to this high aluminium content. Moreover, the lower content in the superconducting phase noted for coatings heat treated for 6 hours is likely to decrease the critical current density J_c .

There are some indications that a liquid phase is formed within coatings during the heat treatment at 950°C . Metallographic examination (Figure 6) of the 6 hour heat treated coating reveals that a material has infiltrated deeply into the substrate cracks. No such infiltrations are

present in as-sprayed samples. Therefore, the infiltration did not take place during the plasma spraying but rather during the heat treatment. Infiltrations are also locally observed for the 15 minute heat treated sample. A second indication for the formation of a liquid phase during the heat treatment can be observed on the initially uncoated surface of the alumina substrate adjacent to the superconducting coating. Indeed, a grey zone is observed near the edge of the superconducting coating on the alumina substrate after the heat treatment. This zone is about 1 mm wide after 15 minutes at 950°C and about 3 mm wide after 6 hours at the same temperature. This indicates that a liquid flowed from the superconducting coating on the alumina substrate during the heat treatment. The surface of this solidified liquid after the 6 hour heat treatment is shown in Figure 6. It contains two different phases. The first one (phase 1 in Figure 6) which covers the alumina substrate and has a white color, is similar to the Al-Ba oxide phase (phase 3) observed in Figures 4-a and 5-a. The second phase (Figure 6) is darker and is composed essentially of copper oxide. This second phase appears as small islands laying on the Al-Ba oxide surface. Less than 1 at. % of yttrium is detected on the surface of the solidified liquid.

X-ray diffraction analysis reveals that BaAl_2O_4 is the only crystalline phase present on the surface of the solidified liquid. Moreover, by mechanically removing the coating heat treated for 6 hours from the alumina substrate, the Al-Ba oxide film is left on the substrate surface and only the BaAl_2O_4 phase is detected by X-ray diffraction analysis. It is worth noting that EDX analyses give an Al-Ba

concentration ratio of about 3:1 in these zones instead of 2:1. This discrepancy may be due to the lack of precision of the EDX analyses or to the presence of another compound not detected by X-ray diffraction.

The infiltrated compound present within the alumina substrate cracks (Figure 6) is an Al-Ba oxide. However, the binary Al_2O_3 -BaO phase diagram indicates that the minimum solidus temperature is found at 1425°C for the $3\text{BaO} \cdot \text{Al}_2\text{O}_3/\text{BaO}$ eutectic (12). Therefore, during the heat treatment at 950°C, the Al-Ba oxide phase is solid and can not infiltrate the alumina substrate cracks. The metallic elements originating from the coating and present in the solidified liquid zone around the superconducting coating are essentially Ba and Cu. Thus, the liquid phase formed at 950°C contains only these elements. Roth and al. (13) have reported that X-ray diffraction peaks of a Ba-Cu-O quenched liquid are detected in $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples quenched from 950-977°C. Moreover, they have shown that a liquid exists above 930°C in $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples slightly enriched in yttrium. There also exists an eutectic between BaCuO_2 and CuO at about 900°C (13,14).

Therefore, we can suggest the following possible sequence of events to explain the phase distribution observed in the heat treated coatings. During the heat treatment, a Ba-Cu-O liquid is formed in the as-sprayed coating. This liquid may flow on the alumina substrate, infiltrate the cracks, and then, react with the alumina forming the Al-Ba oxide. The latter compound is solid at the heat treatment temperature of 950°C. During the Al-Ba oxide formation, the copper oxide accumulates near the

superconducting coating interface and then can diffuse in the coating (Figures 4 and 5). In the uncoated regions of the substrate wetted by the liquid, the copper oxide accumulates at the substrate surface and then agglomerates in small islands as observed in Figure 6. Therefore, barium content in the coating is reduced leading to a decrease in the amount of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ superconducting phase and to the appearance of the $\text{Y}_2\text{Ba}_2\text{CuO}_5$ and CuO phases.

CONCLUSION

$\text{YBa}_2\text{Cu}_3\text{O}_x$ powders have been plasma sprayed on alumina substrates. As-sprayed coatings are not superconducting and must be heat treated at 950°C to restore the superconducting phase. During this heat treatment, interaction between the substrate and the coating occurs leading to a degradation of the coating superconducting properties. The degradation is attributed to the diffusion of aluminium in the superconducting coating and to the formation of a Ba-Cu-O liquid that reacts strongly with the alumina substrate.

It would be possible to minimize the coating degradation by lowering the heat treatment temperature below the minimum solidus temperature of the Y-Ba-Cu oxide system (900°C) avoiding in this way the formation of the Ba-Cu-O liquid. Moreover, according to phase diagrams, the use of a $\text{YBa}_2\text{Cu}_3\text{O}_x$ starting powder enriched in barium increases the solidus temperature and might possibly reduce the formation of a liquid at temperature below 975°C (13).

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Table 1 - Metallic element composition (EDX) of the most important phases denoted in Figure 4-a in coating heat treated for 15 minutes at 950°C.

Phase	Y (at.%)	Ba (at.%)	Cu (at.%)	Al (at.%)	Corresponding phase	
1	a	19.8	31.5	45.5	3.2	YBa ₂ Cu ₃ O _x
	b	18.9	31.3	43.8	6.0	YBa ₂ Cu ₃ O _x
2	46.8	22.8	23.3	7.0	Y ₂ BaCuO ₅	
3	0.0	23.4	1.4	75.2	Al-Ba-O	

a) Near the coating surface.

b) Near the alumina interface.

Table 2 - Metallic element composition (EDX) of the phases denoted in Figure 5-a in coating heat treated for 6 hours at 950°C.

Phase	Y (at.%)	Ba (at.%)	Cu (at.%)	Al (at.%)	Corresponding phase
1					
{ a	20.0	31.0	45.6	3.5	$\text{YBa}_2\text{Cu}_3\text{O}_x$
{ b	19.5	30.7	44.4	5.4	$\text{YBa}_2\text{Cu}_3\text{O}_x$
2	51.8	20.8	20.5	7.2	Y_2BaCuO_5
3	0.0	23.4	2.8	73.8	Al-Ba-O
4	0.0	1.4	94.6	3.7	CuO

a) Near the coating surface.

b) Near the alumina interface.

FIGURE CAPTIONS

Figure 1 - X-ray diffraction patterns of coating surface: a) as-sprayed, and after heat treatments at 950°C for b) 15 minutes, c) 30 minutes and d) 6 hours.

Figure 2 - Relative resistivity of coatings as function of temperature for different heat treatment times: a) 15 minutes, b) 30 minutes and c) 6 hours (ρ_0 is the coating resistivity at 273 K).

Figure 3 - Scanning electron micrograph of an as-sprayed $\text{YBa}_2\text{Cu}_3\text{O}_x$ coating.

Figure 4 - Scanning electron micrograph (a) and corresponding EDX mappings for yttrium (b), barium (c) and copper (d) of a coating heat treated for 15 minutes. (See text for phase identification).

Figure 5 - Scanning electron micrograph (a) and corresponding EDX mappings for yttrium (b), barium (c) and copper (d) of a coating heat treated for 6 hours. (See text for phase identification).

Figure 6 - Scanning electron micrograph of a 6 hour heat treated coating showing the deep infiltration of the Al-Ba-O phase in the alumina substrate cracks.

Figure 7 - Aspect of the solidified liquid zone near the $\text{YBa}_2\text{Cu}_3\text{O}_x$ coating after a 6 hour heat treatment. Zone 1 corresponds to the Al-Ba oxide phase and zone 2 to the CuO islands.













